

# PATENT ABSTRACTS OF JAPAN

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## (54) HYDROGENATION OF HALOKETONE

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a haloalcohol by hydrogenation of a haloketone in the presence of a specific catalyst.

**SOLUTION:** A haloketone (e.g. 2-chloroketone) is hydrogenated using, as catalyst, a ruthenium complex compound bearing a substituted cyclopentadienone compound as ligand [e.g.  $(\text{Ph}_4\text{C}_4\text{CO})_2\text{H}(\mu\text{H})(\text{CO})_4\text{Ru}_2$ ] in a solvent (e.g. toluene) under a hydrogen gas pressure of 0.2-150 bar at 10-200°C for 0.1-50h. The amount of the catalyst to be used is 0.0000001-1mol per mol of the 2chloroketone as the raw material and the catalyst can be used repeatedly. The 2-chloroalcohol obtained by the above hydrogenation is useful as an intermediate for various organic compounds such as medicines and agrochemicals; in particular, 1,3- dichloro-2-propanol obtained by hydrogenation of 1,3-dichloroacetone can be easily dehydrohalogenated by e.g. sodium hydroxide, being useful as an intermediate for epichlorohydrin, a raw material for epoxy resins and synthetic rubbers.

## CLAIMS

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### [Claim(s)]

[Claim 1] The hydrogenation approach of the halogenation ketone characterized by using the ruthenium complex compound which has a permutation cyclo PENTAJI enone compound in a ligand as a catalyst in the approach of hydrogenating a halogenation ketone under existence of a catalyst.

[Claim 2] The hydrogenation approach of a halogenation ketone according to claim 1 that a halogenation ketone is alpha-chloro ketone and a hydrogenation product is alpha-chloro alcohol.

[Claim 3] The hydrogenation approach of a halogenation ketone according to claim 1 that a halogenation ketone is 1 and 3-dichloroacetone and hydrogenation products are 1 and 3-dichloro-2-propanol.

[Claim 4] The hydrogenation approach of a halogenation ketone according to claim 1 that a halogenation ketone is 1-monochloroacetone and a hydrogenation product is 1-chloro-2-propanol.

## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the hydrogenation approach of a halogenation ketone. alpha-chloro alcohol obtained by hydrogenating a halogenation ketone, for example, alpha-chloro ketone, is useful as intermediate field of the various organic compounds which make a remedy and agricultural chemicals the start. Dehydrochlorination is easily possible for especially 1, 1 obtained by hydrogenating 3-dichloroacetone, and 3-dichloro-2-propanol by the sodium hydroxide, the potassium hydroxide, or milk of lime, and they are useful as intermediate fields for manufacture of the epichlorohydrin which is the raw material of an epoxy resin or synthetic rubber.

#### [0002]

[Description of the Prior Art] If ketones and aldehydes are returned, alcohols will be obtained, but since reduction of the part also tends to break out when they include association of carbon and chlorine, and it has the Krol radical especially in the alpha position of a carbonyl group, it is not so easy to return only a carbonyl group part to a hydroxyl group selectively. It is indicated by the U.S. Pat. No. 4,024,193 description about the approach of returning the acetone or acetophenone derivative which has a halogen radical or hydroxyl groups, such as the Krol radical, in an alpha position to the alcoholic body which corresponds a ruthenium triphenyl phosphine complex and by carrying out bottom hydrogen reduction of strong acid existence. However, the ruthenium triphenyl phosphine complex which is a catalyst is used for this patent specification example by 0.012 or more and high concentration by the mole ratio to the raw material ketone body, and when the acetone derivative which has a halogen radical or a hydroxyl group in an alpha position is moreover used for a raw material, the publication of yield, selectivity, etc. is not made. A remarkably low thing becomes clear (example of a

comparison), and this reduction reaction which used the ruthenium triphenyl phosphine complex for the catalyst in our examination has dissatisfied activity as the hydrogenation approach of industrial alpha-chloro ketone.

[0003] The manufacturing method of 1, 1 characterized by making a 3-dichloro acetone and isopropanol react under existence of aluminum isopropoxide, and 3-dichloro-2-propanol is indicated by JP,7-23332,B. The hydrogen atom of isopropanol moves this method to dichloroacetone (it omits Following DCA) by the catalysis of aluminum isopropoxide. Say that DCA is changed into dichloro propanol (it omits Following DCP). well-known e-mail wine-pound RUFUBARI reduction (WAIRUZU for example, A.L. --) Organic The 2nd volume (Organic Reactions) of rear KUSHONZU, the 178page(1944); - - JONWAIRI and -- Suns and an in corporation (New York) (JOHNWILEY & SONS, INC (New York)) are used.

[0004] Although the reduction reaction using this aluminum isopropoxide gives the object DCP with high selectivity, since moisture decomposes the aluminum isopropoxide of a catalyst and that decomposition product induces side reaction, such as DCA and decomposition of DCP, further, it is necessary to reduce mixing of the moisture into a system as much as possible during a reduction reaction. Moreover, although the mole ratio of the aluminum isopropoxide to DCA is an example of an activity with desirable 0.01-1, when the mole ratio of the aluminum isopropoxide to DCA reacts by 0.01 as indicated by JP,7-23332,B, a reaction rate falls remarkably.

[0005]

[Problem(s) to be Solved by the Invention] Like the above, the above-mentioned approach uses aluminum isopropoxide for a catalyst. Dehydration processing is performed in advance of a reaction, and the isopropanol which uses a catalyst with a comparatively expensive large quantity in order to manufacture DCP, and usually contains about hundreds of ppm moisture is reduced to about dozens of ppm, It is necessary to manage strictly so that the amount of reaction implementation Nakamizu may not mix in a list, and there is a trouble that it is not what can be satisfied as the industrial manufacture approach of DCP. The object of this invention is to offer the approach of hydrogenating a halogenation ketone advantageously industrially and manufacturing corresponding halogenation alcohol.

[0006]

[Means for Solving the Problem] It was stable with moisture, oxygen, or heat contained in the system of reaction in order that this invention person etc. may solve the above-mentioned technical problem, and was mild conditions, and as a result of examining various hydrogenation catalysts for halogenation ketones which have high activity and have high selectivity to a carbonyl group, it came to complete header this invention for a technical problem being solved by using the ruthenium complex which has a permutation cyclo PENTAJI enone compound in a ligand as a hydrogenation catalyst. That is, this invention is in the hydrogenation approach of the halogenation ketone characterized by using the ruthenium complex compound which has a permutation cyclo PENTAJI enone compound in a ligand as a catalyst in the approach of hydrogenating a halogenation ketone under existence of a catalyst. In addition, the example which manufactured alpha-chloro alcohol which returns alpha-chloro ketone and corresponds is not known to current, using the ruthenium complex which has a permutation cyclo PENTAJI enone compound in a ligand as a hydrogenation catalyst. Hereafter, the hydrogenation approach

of this invention is explained to a detail.

[0007]

[Embodiment of the Invention]

(Raw material) A chloro ketone is desirable in the halogenation ketone used as a raw material in this invention, and since especially this invention is suitable in the case of alpha-chloro ketone, this invention is hereafter explained to an example for alpha-chloro ketone. alpha-chloro ketone of a raw material means the ketone by which the Krol radical was introduced into the contiguity carbon of a carbonyl group. Especially the number of the Krol radicals introduced does not receive a limit, but is usually shown by the integer of 1 to 6. the substituent of the ends of a carbonyl group -- the combination of the combination of an alkyl group and an alkyl group and an alkyl group, and an aryl group -- neither interferes. As this alpha-chloro ketone, 1-monochloroacetone, 1, 3-dichloroacetone, 1-chloro-2-propanone, 2-chloro-3-propanone, 1, 3-dichloro-2-propanone, alpha-chloroacetophenone, 2-chloro cyclohexanone, 2, 6-dichloro cyclohexanone, 1 and 1-dichloroacetone, 1 and 1, 1-TORIKURORO acetone, 1 and 1, 3-TORIKURORO acetone, 1, 1 and 3, 3-tetra-monochloroacetone, hexachloroacetone, etc. are mentioned. According to this invention, the alpha-chloro alcoholic body which corresponds by using starting alpha-chloro ketone as a raw material is acquired by high yield. Preferably, as an alpha-chloro ketone which is the case where alpha-chloro ketone by which the one-piece Krol radical was introduced into contiguity carbon is used as a raw material, and starts, 1-monochloroacetone, 1, 3-dichloroacetone, 1-chloro-2-propanone, 2-chloro-3-propanone, 1, 3-dichloro-2-propanone, alpha-chloroacetophenone, 2-chloro cyclohexanone, 2, and 6-dichloro cyclohexanone etc. is mentioned. especially -- desirable -- 1-monochloroacetone, 1, and 3-dichloroacetone -- it is -- mild conditions -- activity and selectivity -- the alpha-chloro alcoholic body which corresponds highly can be acquired by high yield.

[0008] Generally a raw material alpha-chloro ketone can be easily manufactured by chloro-izing a ketone by chlorination agents, such as chlorine gas, a sulfonyl chloride, and a copper(II) chloride, although it is manufactured by the location of the carbon which the Krol radical permutes etc. by various approaches when the substituent of whenever [ permutation / of the Krol radical ], and the ends of a carbonyl group is the combination of an alkyl group and an alkyl group. for example, 1-monochloroacetone -- the reaction (for example, JP,62-134178,A) of an acetone and chlorine gas -- moreover, 1 and 3-dichloroacetone can be manufactured industrially (for example, JP,7-23332,B and JP,54-130511,A each official report) by the reaction of an iodine chloride or the bottom acetone of iodine existence, and chlorine gas.

[0009] (Catalyst) The ruthenium complex compound which has a permutation cyclo PENTAJI enone compound in a ligand as a catalyst in the approach of this invention is used. The permutation cyclo PENTAJI enone used as a ligand here means 2, 2 of 4-cyclo PENTAJI enone, 3, and the compound with which the substituent was introduced into the 4 or 5th place, and a substituent does not interfere, no matter what substituents, such as hydrogen, a halogen, alkyl, and aryl, may be introduced. It is an alkyl group and an aryl group preferably, and is the phenyl group which has a phenyl group and a substituent, or a functional group preferably especially, and is a fluoro alkyl group. As such a substituent, phenyl, 4-chlorophenyl, 4-methoxyphenyl, 4-fluoro phenyl, 2, 4-chlorophenyl, 2, 4-methoxyphenyl, 2, 4-fluoro phenyl, trifluoromethyl, pentafluoro ethyl,

etc. are mentioned. The ruthenium complex compound which has these in a ligand shows high activity and hydrogenation selectivity on mild conditions.

[0010] Moreover, even if the class of substituent introduced has 2, 3, and the same each of the 4 or 5th place and they differ again, it does not interfere. Although some are already known as a single nucleus and polynuclear complex about this ruthenium complex compound, by the approach of this invention, these well-known rutheniums complex compound is conventionally usable. Specifically 2 (Ph<sub>4</sub> C<sub>4</sub> CO) H(micro-H) (CO) 4 Ru<sub>2</sub>, (Ph<sub>4</sub> C<sub>4</sub> CO) Ru (CO)<sub>3</sub> and [(CF<sub>3</sub>) C<sub>4</sub> 4 CO] Ru (CO) -- three -- [(4-ClC six H<sub>4</sub>) C<sub>4</sub> 4 CO] Ru (CO)<sub>3</sub> and [2, 5-(C six H<sub>4</sub>) 2-3, and 4-(4-MeOC six H<sub>4</sub>)<sub>2</sub> C<sub>4</sub> CO] Ru (CO) -- three -- [2, 5-(C six H<sub>4</sub>) 2-3, and 4-(4-FC six H<sub>4</sub>)<sub>2</sub> C<sub>4</sub> CO] Ru (CO) -- three -- [(4-ClC six H<sub>4</sub>) C<sub>4</sub> 4 CO] 2 H(micro-H) (CO) 4 Ru<sub>2</sub>, [2, 5-(C six H<sub>4</sub>) 2-3, and 4-(4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> C<sub>4</sub>CO] 2 H(micro-H) (CO) 4 Ru<sub>2</sub>, [2, 5-(C six H<sub>4</sub>) 2-3, and 4-(4-FC six H<sub>4</sub>)<sub>2</sub> C<sub>4</sub> CO] 2 H(micro-H) (CO) 4 Ru<sub>2</sub> grade is mentioned. These are compoundable by the well-known approach (for example, the 10th volume (Organo metallics) of ORGANO METARIKKUSU, such as N. MENASHU, the 3885th page (1991)). Moreover, the ruthenium complex compound which has in a ligand the permutation cyclo PENTAJI enone compound which is not reported until now can also be used. A ruthenium complex compound mainly means the compound with which the ruthenium and the organic radical (ligand) were connected by direct coupling of metal-carbon, although the organometallic compound of a ruthenium is meant and the definition is known widely now (for example, the 1991 Shokabo Publishing issuance, Akio Yamamoto work, the 6th page of organic metal chemistry). Especially the formal oxidation number of the ruthenium atom in the ruthenium complex compound which can be used is not limited, and the class of organic radical which are ligands other than a permutation cyclo PENTAJI enone compound, and a number are not limited. As this ruthenium ligand, a carbon monoxide, a halogen, and a hydride are desirable. Especially a carbon monoxide and a hydride are desirable and an oxidation esterification reaction advances efficiently on mild conditions. the amount of the catalyst used -- alpha-chloro ketone of a raw material -- receiving -- 0.0000001-1 (mole ratio) -- it is the range of 0.000001-0.01 (mole ratio) preferably. It dissociates by general approaches, such as a resultant, distillation, and an extract, and a catalyst can be used repeatedly.

[0011] (Solvent) Although especially the reaction of this invention can be carried out without using a solvent, since the ruthenium complex compound to be used dissolves this in a raw material alpha-chloro ketone in a poorly soluble case, it can be carried out in a suitable solvent if needed for other. As these solvents, ester, such as ether; ethyl acetate, such as hydrocarbons; diethylether, such as a hexane, benzene, and toluene, dimethoxyethane, a tetrahydrofuran, and dioxane, butyl acetate, and a butyrolactone, can be mentioned, for example. The amount of these solvents used of especially a limit is [ nothing ] and is arbitrary.

[0012] (The reaction approach) This reaction is carried out under hydrogen gas existence. At least one or less atmospheric pressure of partial pressures of hydrogen gas may be enough carried out under a pressure with a reaction higher than usual although it goes on, in order to obtain a higher reaction rate. Moreover, in order to make selectivity of hydrogenation of the carbonyl group of alpha-chloro ketone into sufficient thing, it is not desirable to adopt a not much high pressure. Therefore, the range of 0.2-150 bars of pressures of the hydrogen gas usually carried out is 0.5-100 bars preferably. In addition,

even if purity of hydrogen gas is not necessarily high, it can mix the inert gas which does not block an intentional neurosis if needed, for example, nitrogen, a carbon dioxide, an argon, etc. at a rate of arbitration.

[0013] Although progress of a reaction is accepted also at a room temperature, in order to obtain a higher reaction rate, it usually carries out under heating. Generally the range of 10-200 degrees C of reaction temperature is 20-150 degrees C preferably. Since reaction time changes with the conditions of a reaction, it is considered that the event of generally absorption of gas no longer being accepted is the ending point of a reaction. Generally, it is the range of 0.2 - 30 hours preferably for 0.1 to 50 hours.

[0014] The resultant acquired by the manufacture approach of this invention is alpha-chloro alcohol. Furthermore, it is alpha-chloro alcohol which the carbonyl group of alpha-chloro ketone is hydrogenated and is produced by becoming a hydroxyl group in detail and which is secondary alcohol and has the Krol radical originating in a raw material alpha-chloro ketone to the contiguity carbon of a hydroxyl group. \*\*\*\*\* generation of the dechlorination object in accordance with reduction of the Krol radical cannot be carried out, but it can acquire the object alpha-chloro alcoholic body by high selectivity and high yield. Separation of the product from a reaction mixture including a catalyst can be performed by well-known approaches, such as distillation, an extract, and adsorption.

[0015]

[Example] This invention is not limited by these examples, although an example is given to below and the approach of this invention is explained to it still more concretely. In addition, quantitative analysis of the product was carried out with the internal standardization which used the nonane as the internal standard matter using the gas chromatography, and it asked for an invert ratio and selectivity by the bottom type.

[0016]

[Equation 1]

$$\text{転化率} = 100 \times \frac{\text{反応した}\alpha\text{-クロロケトン (モル数)}}{\text{仕込んだ}\alpha\text{-クロロケトン (モル数)}}$$

[0017]

[Equation 2]

$$\text{選択率 (\%)} = 100 \times \frac{\text{生成した}\alpha\text{-クロロアルコール (モル数)}}{\text{反応した}\alpha\text{-クロロケトン (モル数)}}$$

Moreover, the turnover number used in the example was calculated according to the bottom type.

[0018]

[Equation 3]

$$\text{ターンオーバー数} = \frac{\text{生成した}\alpha\text{-クロロアルコール (モル数)}}{\text{仕込んだルテニウム触媒のモル数}}$$

[0019] To the glass autoclave of 100ml of example 1 content volume, a churning child, 2

(Ph<sub>4</sub> C<sub>4</sub> CO) H(micro-H) (CO)<sub>4</sub> Ru<sub>2</sub> 3.5mg (0.0034 millimol), After teaching and sealing nonane 0.17g as toluene 2.69g and internal standard matter for analysis as 1 and 3-dichloroacetone 884.5mg (6.90 millimol) and a solvent and hydrogen gas permuted the system bashful phase, this gas was pressed fit to 4 bars. The reaction of 3.5 hours was performed at 80 degrees C, agitating. In the meantime, the gas absorbed was supplied from the outside and maintained the pressure of a reactor at the predetermined pressure. The quantum of the uniform solution which cooled, opened and obtained the reactor to the room temperature was carried out with the gas chromatography. Consequently, 1 and 3-dichloroacetone disappeared thoroughly and 1 and 3-dichloro-2-propanol 884.5mg (6.76 millimol) generated it. The invert ratio of a raw material 1 and 3-dichloroacetone was 100%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 1987 (a mol/mol) 98.0% again.

[0020] To the autoclave made from example 2 stainless steel (30ml of content volume), a churning child, 2 H(micro-H) (CO)<sub>4</sub> Ru<sub>2</sub> 3.7mg (0.0036 millimol), (Ph<sub>4</sub> C<sub>4</sub> CO) After teaching and sealing nonane 0.20g as toluene 2.86g and internal standard matter for analysis as 1 and 3-dichloroacetone 871.5mg (6.79 millimol) and a solvent and hydrogen gas permuted the system bashful phase, this gas was pressed fit to 8 bars. The reaction of 1.5 hours was performed at 80 degrees C, agitating. In the meantime, the gas absorbed was supplied from the outside and maintained the pressure of a reactor at the predetermined pressure. The quantum of the uniform solution which cooled, opened and obtained the reactor to the room temperature was carried out with the gas chromatography. Consequently, 1 and 3-dichloroacetone disappeared thoroughly and 1 and 3-dichloro-2-propanol 811.2mg (6.29 millimol) generated it. The invert ratio of a raw material 1 and 3-dichloroacetone was 100%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 1749 (a mol/mol) 92.6% again.

[0021] To the autoclave made from example 3 stainless steel (30ml of content volume), a churning child, 2 H(micro-H) (CO)<sub>4</sub> Ru<sub>2</sub> 1.5mg (0.0015 millimol), (Ph<sub>4</sub> C<sub>4</sub> CO) After teaching and sealing nonane 0.24g as toluene 8.81g and internal standard matter for analysis as 1, 1899.0 mg (14. 80 millimol) 3-dichloroacetone, and a solvent and hydrogen gas permuted the system bashful phase, this gas was pressed fit to 40 bars. The reaction of 7.0 hours was performed at 80 degrees C, agitating. In the meantime, the gas absorbed was supplied from the outside and maintained the pressure of a reactor at the predetermined pressure. The quantum of the uniform solution which cooled, opened and obtained the reactor to the room temperature was carried out with the gas chromatography. Consequently, 1 and 3-dichloroacetone 343.0mg (2.70 millimol), 1, and 1420.6 mg (11. 01 millimol) 3-dichloro-2-propanol generated. The invert ratio of a raw material 1 and 3-dichloroacetone was 91.0%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 7555 (a mol/mol) 91.0% again.

[0022] To the autoclave made from example 4 stainless steel (30ml of content volume), a churning child, 2 H(micro-H) (CO)<sub>4</sub> Ru<sub>2</sub> 1.5mg (0.0015 millimol), (Ph<sub>4</sub> C<sub>4</sub> CO) After teaching and sealing nonane 0.24g as toluene 7.85g and internal standard matter for analysis as 1, 1895.6 mg (14. 78 millimol) 3-dichloroacetone, and a solvent and hydrogen gas permuted the system bashful phase, this gas was pressed fit to 100 bars. The reaction of 6.0 hours was performed at 80 degrees C, agitating. In the meantime, the gas absorbed was supplied from the outside and maintained the pressure of a reactor at the predetermined pressure. The quantum of the uniform solution which cooled, opened and

obtained the reactor to the room temperature was carried out with the gas chromatography. Consequently, 1 and 3-dichloroacetone 542.9mg (4.27 millimol), 1, and 1263.0 mg (9.79 millimol) 3-dichloro-2-propanol generated. The invert ratio of a raw material 1 and 3-dichloroacetone was 71.1%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 6718 (a mol/mol) 91.0% again.

[0023] To an example 5 glass autoclave (100ml of content volume), a churning child, 2 H(micro-H) (CO)<sub>4</sub> Ru<sub>2</sub> 3.5mg (0.0034 millimol), (Ph<sub>4</sub> C<sub>4</sub> CO) After teaching and sealing nonane 0.19g as toluene 4.17g and internal standard matter for analysis as 1 and 3-dichloroacetone 865.2mg (6.74 millimol) and a solvent and hydrogen gas permuted the system bashful phase, this gas was pressed fit to 10 bars. The reaction of 6.0 hours was performed at 50 degrees C, agitating. In the meantime, the gas absorbed was supplied from the outside and maintained the pressure of a reactor at the predetermined pressure. Quantitative analysis by the gas chromatography of the sample which cooled the reactor to the room temperature and was extracted under the nitrogen air current was carried out. Consequently, 1 and 3-dichloroacetone 27.1mg (0.21 millimol), 1, and 3-dichloro-2-propanol 772.53mg (5.99 millimol) generated. The invert ratio of a raw material 1 and 3-dichloroacetone was 91.0%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 1761 (a mol/mol) 91.7% again.

[0024] 1 and 3-dichloroacetone 875.0mg (6.89 millimol) dissolved in toluene 1.55g was added to this reaction mixture, it pretreated to it by the same actuation as the above, and the hydrogen gas pressure of 10 bars, 50 degrees C, and a 8.0-hour reaction were performed to it. Quantitative analysis of the sample which cooled the reactor to the room temperature and was extracted under the nitrogen air current was carried out with the gas chromatography. Consequently, 1 and 3-dichloroacetone disappeared thoroughly and 1 and 1702.0 mg (13. 19 millimol) 3-dichloro-2-propanol were generating it by the total. The invert ratio of a raw material 1 and 3-dichloroacetone was 100.0%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 3880 (a mol/mol) 97.3% again. Furthermore, in addition to 1 dissolved in toluene 1.77g, and 3-dichloroacetone 883.0mg (6.95 millimol) reaction mixture, it pretreated by the same actuation as the above, and the hydrogen gas pressure of 10 bars, 50 degrees C, and a 7.0-hour reaction were performed. Quantitative analysis of the sample which cooled the reactor to the room temperature and was extracted under the nitrogen air current was carried out with the gas chromatography. Consequently, 1 and 3-dichloroacetone disappeared thoroughly and 1 and 2559.5 mg (19. 84 millimol) 3-dichloro-2-propanol were generating it by the total. The invert ratio of a raw material 1 and 3-dichloroacetone was 100.0%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 5834 (a mol/mol) 97.0% again.

[0025] 1 and 3-dichloroacetone 2227mg (17.53 millimol) dissolved in toluene 3.89g was added to this reaction mixture, it pretreated to it by the same actuation as the above, and the hydrogen gas pressure of 10 bars, 50 degrees C, and a 12.0-hour reaction were performed to it. Quantitative analysis of the sample which cooled the reactor to the room temperature and was extracted under the nitrogen air current was carried out with the gas chromatography. Consequently, 1 and 3-dichloroacetone disappeared thoroughly and 1 and 4560.4 mg (35. 35 millimol) 3-dichloro-2-propanol were generating it by the total. The invert ratio of a raw material 1 and 3-dichloroacetone was 100.0%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 10395 (a mol/mol) 93.5%



again.

[0026] To the autoclave made from example 6 stainless steel (30ml of content volume), a churning child, 2 H(micro-H) (CO)<sub>4</sub> Ru<sub>2</sub> 3.5mg (0.0034 millimol), (Ph<sub>4</sub> C<sub>4</sub> CO) After teaching and sealing nonane 0.20g as toluene 2.85g and internal standard matter for analysis as 1-monochloroacetone 641.4mg (6.59 millimol) and a solvent and hydrogen gas permuted the system bashful phase, this gas was pressed fit to 8 bars. The reaction of 4.0 hours was performed at 80 degrees C, agitating. In the meantime, the gas absorbed was supplied from the outside and maintained the pressure of a reactor at the predetermined pressure. The quantum of the uniform solution which cooled, opened and obtained the reactor to the room temperature was carried out with the gas chromatography. Consequently, 1-monochloroacetone 149.2mg (1.61 millimol) and 1-chloro-2-propanol 462.3mg (4.89 millimol) generated. The invert ratio of raw material 1-monochloroacetone was 75.5%, and the turnover number of the selectivity of 1-chloro-2-propanol was 1438 (a mol/mol) 98.3% again.

[0027] To an example of comparison 1 glass autoclave (100ml of content volume), a churning child, RuCl<sub>2</sub> 3 (PPh<sub>3</sub>) 15.1mg (0.0158 millimol), as 1 and 3-dichloroacetone 757.1mg (5.90 millimol), 1000mg of water, and a solvent -- N-methyl pyrrolidone 4.95g, 2-methoxyethanol 7.11g, and analysis -- business -- as internal standard matter After teaching and sealing nonane 0.22g and hydrogen gas permuted the system bashful phase, this gas was pressed fit to 5 bars. The reaction of 4.0 hours was performed at 80 degrees C, agitating. In the meantime, the gas absorbed was supplied from the outside and maintained the pressure of a reactor at the predetermined pressure. Quantitative analysis by the gas chromatography of the sample which cooled the reactor to the room temperature and was extracted under the nitrogen air current was carried out. Consequently, 1 and 3-dichloroacetone 747.6mg (5.89 millimol), 1, and 3-dichloro-2-propanol were not generated. The invert ratio of a raw material 1 and 3-dichloroacetone was 0.26%, and the turnover number of the selectivity of 1 and 3-dichloro-2-propanol was 0 (a mol/mol) 0% again.

[0028]

[Effect of the Invention] According to the approach of this invention, it becomes possible on mild conditions to hydrogenate a halogenation ketone, especially alpha-chloro ketone advantageously industrially, and alpha-chloro alcohol which corresponds by this can be manufactured.

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[Translation done.]